

# Evaluation of the wetting time of porous electrodes in electrolytic solutions containing ionic liquid

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**Abstract** The wetting time of porous electrodes with electrolytes based on organic solvents and ionic liquids, respectively, was investigated with two different techniques: with a tensiometer and by impedance spectroscopy. The results of this study showed that the wetting time of a porous electrode with ionic liquid-based electrolytes is up to 20 times longer than that with electrolytes comprising organic solvents. A significant reduction in the wetting time with ionic liquid-based electrolytes could be achieved by adding organic solvents. This effect can be explained by the interplay of reduced viscosity, increased surface tension and change in contact angle caused by the addition of the organic solvent, with the lower viscosity being the main driver of improved wetting kinetics.

**Keywords** Electrode wetting · Ionic liquid · Propylene carbonate · Mixtures · Lithium iron phosphate

## 1 Introduction

Current electrolyte systems for commercially available lithium-ion batteries (LIBs) are usually based on mixtures of cyclic and linear organic carbonates, for example, propylene carbonate (PC), ethylene carbonate (EC) and dimethyl carbonate (DMC) as solvent. The use of these

mixtures allows the realization of high-performance batteries. However, due to the low boiling point of linear carbonates, the operative temperature range of LIBs is limited. Additionally, linear carbonates display low flash points, which pose the problem of serious safety risks [1, 2]. Therefore, since several years, considerable research has been focused on the development of alternative electrolytes with improved safety and an extended operative temperature range.

Ionic liquids (ILs) are currently considered as one of the most attractive candidates to replace organic carbonates as electrolyte solvents in next-generation LIBs. The main advantages of ILs compared to organic carbonates are their nonflammability, their negligible vapor pressure and their high chemical and thermal stability [3, 4]. Several studies showed that ILs can be successfully used as electrolyte solvents for LIBs [5–8].

However, for the realization of high-performance LIBs, several aspects need to be carefully considered [9]. One of these aspects is the speed with which the electrodes are wetted by the electrolyte. This is of particular importance for the manufacturing of LIBs. Therefore, the behavior of electrolytes in terms of electrode wetting needs to be investigated when new solvents like ILs are used.

So far, there are only a few papers reporting on the wettability of electrodes by electrolytes. In 2004, Wu et al. [10] described the wetting of lithium cobalt oxide (LiCoO<sub>2</sub>) and mesocarbon microbead (MCMB) electrodes in different conventional electrolytes. More recently, Stefan et al. investigated the wetting of separators (Celgard, Separion) and electrodes (LiCoO<sub>2</sub>, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, graphite) by ILs based on the TFSI anion, and Dahbi et al. reported on interfacial properties of graphite electrodes and Celgard separators using conventional electrolytes [11, 12]. However, to the best of our knowledge, no comparative study

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on the wetting properties of porous electrodes in electrolytes based on organic solvents and ILs, respectively, has been published up to now. Such a comparative study can give insight into the dependence of the wetting behavior of electrodes on the employed electrolyte solvent.

In this study, we investigated the influence of the electrolyte composition on the wetting behavior of lithium iron phosphate ( $\text{LiFePO}_4$ ) composite electrodes. The wetting process was studied in electrolytes based on PC and the IL *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ( $\text{PYR}_{14}\text{TFSI}$ ), both containing lithium bis(trifluoromethanesulfonyl)imide ( $\text{LiTFSI}$ ) as Li salt. Moreover, three ternary mixtures of  $\text{PC-PYR}_{14}\text{TFSI-LiTFSI}$  were studied in order to understand the influence of the addition of ILs to organic carbonates on the wetting process. Recently, it was shown that such mixtures are very interesting candidates for use as electrolytes in LIBs as they allow better performances at room temperature and high current rates compared to electrolytes based on pure ILs [5]. Another advantage of these mixtures is that their properties (e.g., conductivity and viscosity) can be tailored by varying the ratio between IL and organic carbonates [13–18].

At the beginning of the paper, surface tension, viscosity and density of the different electrolytes are compared followed by the characterization of the  $\text{LiFePO}_4$  composite electrodes in terms of porosity, pore size distribution and morphology. Afterward, the wetting behavior of the  $\text{LiFePO}_4$  composite electrodes with the different electrolytes is investigated using a tensiometer and impedance spectroscopy. Finally, a statement about the pros and cons of the two methods is given, based on the obtained results.

## 2 Experimental

### 2.1 Electrolyte preparation

Propylene carbonate (UBE, Japan) was used as received.  $\text{PYR}_{14}\text{TFSI}$  was synthesized according to the procedure reported earlier [18]. Three electrolytes based on mixtures of PC and  $\text{PYR}_{14}\text{TFSI}$ , and two electrolytes containing the pure solvents with  $\text{LiTFSI}$  (3 M battery grade) as lithium salt were prepared. A concentration of 0.3 M  $\text{LiTFSI}$  was used for the  $\text{PYR}_{14}\text{TFSI}$ -based electrolyte as a compromise regarding conductivity and availability of  $\text{Li}^+$ . For the sake of comparability, all the other electrolytes were prepared with the same concentration of Li salt. In the following, the electrolyte solvent compositions are always given in weight percentage with respect to the total amount of solvent. The water content of all prepared electrolytes was below 10 ppm, as measured with coulometric Karl Fischer titration (Mettler Toledo C30).

### 2.2 Physicochemical characterization of the electrolytes

Surface tension was measured with a KRÜSS DSA100 drop shape analyzer using the sessile drop method at room temperature (ca. 20 °C). The reported values are arithmetic averages of at least 10 measurements for each electrolyte. The drop shape analyzer was located in a dry room. Hence, the reported values of surface tension are valid for dry air atmosphere. Viscosity was measured at 20 °C using an Anton-Paar Physica MCR 301 rheometer with cone-plate geometry. A rotating cone with a diameter of 50 mm and an angle of 0.5° was used. The shear rate was individually chosen for each electrolyte depending on its viscosity to operate the cone with optimal shear rate for each viscosity. The shear rate was set to 1,000, 3,000, 4,000, 6,000 and 8,000  $\text{s}^{-1}$  for the  $\text{PC-PYR}_{14}\text{TFSI-0.3 M LiTFSI}$  mixtures with 0, 20, 50, 80 and 100 wt% PC content, respectively. Density values at 20 °C were determined with a Mettler Toledo DE40 density meter.

### 2.3 Electrode preparation

$\text{LiFePO}_4$  composite electrodes were prepared using a testing-scale battery line. The dry composition of the electrodes was as follows: 88 wt% carbon-coated  $\text{LiFePO}_4$  (type P2, Süd-Chemie), 6 wt% carbon black (Super C65, TIMCAL) and 6 wt% polyvinylidene fluoride (PVdF) binder (KF Polymer W#1100, Kureha). The electrodes were casted on Al foil (20  $\mu\text{m}$ , high purity, Schlenk, Germany). Squared electrodes (18 × 18 mm) and disk electrodes (12 mm diameter) were punched out of the obtained electrode sheets and dried at 120 °C under vacuum overnight. The active mass loading of the electrodes was approximately 10  $\text{mg cm}^{-2}$ . Porosity and pore size distribution of the electrodes were measured by mercury porosimetry (Porotec Pascal 440). SEM images of the electrodes were taken with an Auriga scanning electron microscope (Carl Zeiss) using an acceleration voltage of 5 kV, working distance of 1.9 mm and a magnification of 20,000 times.

### 2.4 Evaluation of the electrode wetting

Two different techniques, employing a tensiometer and impedance spectroscopy, respectively, were used to investigate the wetting behavior of  $\text{LiFePO}_4$  composite electrodes in the before-mentioned electrolytes.

Method 1: Tensiometer: The wetting of the electrodes was investigated gravimetrically with a KRÜSS K100 tensiometer according to an experiment described by Lundblad et al. [19]. Squared electrodes (18 × 18 mm) were brought into contact with the electrolyte, and the

weight increase caused by the wetting of the pores of the electrodes was measured continuously with the high-precision balance of the tensiometer. A common way to describe the wetting process of a porous medium (e.g., a composite electrode) is to consider the porous structure as an ensemble of capillaries. Under this assumption, the wetting process can be described by the relations known for capillary imbibition. Capillary rise is a nonlinear process whose complete description is not trivial. Fortunately, simplifications can be made for the flow regime where inertia and gravity influences can be neglected. In this case, the capillary flow can be described by the Lucas–Washburn equation (Eqs. 1a and 1b) [20, 21].

$$h(t) = K\sqrt{t} \quad (1a)$$

$$K = \sqrt{\left(\frac{r\sigma \cos \theta}{2\eta}\right)} \quad (1b)$$

In Eq. 1a,  $h$  is the current height of the rising fluid,  $t$  is the passed imbibition time, and the proportionality constant  $K$ , also called penetrability, is a measure for the speed of wetting. In Eq. 1b,  $r$  is the pore radius of the capillary,  $\sigma$  the surface tension of the fluid,  $\theta$  the three-phase contact angle between capillary, fluid and atmosphere and  $\eta$  the viscosity of the fluid.  $K$  can be determined from a linear regression in an  $h$  versus  $t^{1/2}$  plot.

The square-root dependence between penetration height and imbibition time is strictly valid only for straight vertical capillaries. In a porous medium the effect of tortuosity cannot be neglected and time exponents  $<0.5$  are often found. Cai et al. [22] derived a model to estimate the time exponent from porosity and minimal and maximal pore diameter. They also showed that a higher porosity usually corresponds to a higher time exponent. For porosities  $>50\%$ , the time exponent was generally found to be close to 0.5. Since the porosity of the investigated composite electrodes was 53.2 %, we decided to use the square-root dependence of Eq. 1a also for this work. To apply the Lucas–Washburn equation, the measured mass increase  $\Delta m$  during the imbibition process (measured with the tensiometer) can be converted to a height increase in the moving electrolyte front by dividing the measured mass increase  $\Delta m$  by the density  $\rho$  of the electrolyte and the cross section  $A$  and porosity  $P$  of the porous layer of the electrode (Eq. 2).

$$h = \frac{1}{\rho AP} \Delta m \quad (2)$$

The tensiometer was equipped with a temperature chamber set to 20 °C, and the electrolyte was thermally equilibrated for 30 min before starting the measurement. The penetrability measurements were repeated 3–7 times, and arithmetic averages of the obtained values were calculated.

**Method 2: Impedance spectroscopy:** Two-electrode Swagelok cells comprising the composite electrode as working electrode and a Ni foil (50  $\mu\text{m}$ , high purity, Schlenk, Germany) as counterelectrode were assembled in a MBRAUN glove box ( $\text{H}_2\text{O}$  and  $\text{O}_2$  levels  $<1$  ppm). The electrodes were separated by a Whatman GF/D glass fiber separator soaked with 100  $\mu\text{l}$  of electrolyte. The cells were placed in a Binder MK53 climatic chamber set to 20 °C. Impedance spectra of the cells were measured every hour with a Solartron model 1260A impedance/gain-phase analyzer coupled with a Solartron model 1287A potentiostat/galvanostat controlled by ZPlot (Scribner Associates). A frequency range of 1 MHz–100 mHz and an amplitude of 10 mV were used. As illustrated by Wu et al. [10], the time needed for the impedance to stabilize can be interpreted as the time till the electrodes are fully wetted by the electrolyte. A decrease in the real part of the impedance  $R$  in the high frequency range at the intercept of the impedance with the real axes, which is directly related to the electrolyte conductivity, was observed over time. It was pointed out that this decrease can only originate from an increased contact area between the electrolyte and the electrode, thus a progressed wetting. This can be explained using Eq. 3, the standard equation for electrolyte resistance in a two-plate arrangement where  $\sigma$  is the conductivity of the electrolyte,  $L$  the distance between the two electrodes,  $R$  the resistance of the electrolyte and  $A$  the electrode area. As the conductivity of the electrolyte is not changing with time and the distance between the two electrodes was fixed, a decrease in resistance can be only caused by an increase in the electrode area.

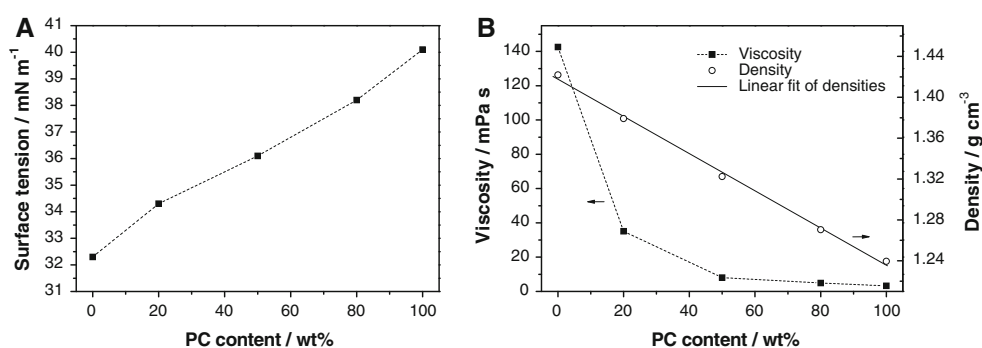
$$\sigma = \frac{L}{R \times A} \quad (3)$$

The wetting tests employing impedance spectroscopy were repeated 3–4 times, and arithmetic averages of the obtained values were calculated. The standard deviation of the wetting times obtained from impedance measurements was typically 3 h.

### 3 Results and discussion

The wetting process of  $\text{LiFePO}_4$  composite electrodes with electrolytes comprising different ratios of organic carbonate and IL as solvents was studied with two different techniques: the tensiometer method and by impedance spectroscopy. As described in the experimental part, for the tensiometer method the Lucas–Washburn relation applies (Eqs. 1a and 1b). Therefore, it is possible to estimate the influence of the electrolyte properties on the penetrability  $K$  (representing the kinetics of the wetting process) independently of the characteristics of the electrode using Eq. 4

**Fig. 1** **a** Surface tension and **b** viscosity (filled squares) and density (open circles) of PC–PYR<sub>14</sub>TFSI–0.3 M LiTFSI mixtures at 20 °C. The dashed lines are only guides to the eye



where  $\sigma$  and  $\eta$  are the surface tension and the viscosity of the different electrolyte mixtures, respectively.

$$K \propto \sqrt{\frac{\sigma}{2\eta}} \quad (4)$$

In order to be able to estimate the influence of the electrolyte properties on  $K$ , the properties of the electrolyte mixtures with different PC-to-PYR<sub>14</sub>TFSI ratios ranging from 0 to 100 % PC were determined. In Fig. 1, the dependence of the surface tension, the viscosity and the density of the electrolytes on the PC fraction of the ternary mixtures PC–PYR<sub>14</sub>TFSI–0.3 M LiTFSI at 20 °C is shown. It can be seen in Fig. 1a that the surface tension of the investigated PC–PYR<sub>14</sub>TFSI–0.3 M LiTFSI mixtures showed nearly linear dependence on the PC fraction of the mixtures. The electrolytes comprising pure solvent, PYR<sub>14</sub>TFSI–0.3 M LiTFSI and PC–0.3 M LiTFSI, displayed a surface tension of 32.3 and 40.1 mN m<sup>-1</sup>, respectively. The surface tensions of the mixtures showed just small deviations from the arithmetic averages. In Fig. 1b, it is shown that the viscosity is strongly decreasing upon addition of PC. While the electrolyte comprising pure PYR<sub>14</sub>TFSI showed a viscosity of 143 mPa s, the mixture containing 20 wt% PC and 80 wt% PYR<sub>14</sub>TFSI displayed a moderately high viscosity of 35.1 mPa s. Further addition of PC led to a reduction in the viscosity to values in the same order of magnitude like one of the electrolyte containing pure PC.

Using Eq. 4, the influence of the electrolyte properties on the penetrability was estimated. In Table 1, the obtained values for  $[\sigma/(2\eta)]^{1/2}$  are reported. Accordingly, a strong influence of the electrolyte properties on the penetrability can be expected. A factor of 7 between the highest expected value of penetrability for PC–0.3 M LiTFSI and the lowest for PYR<sub>14</sub>TFSI–0.3 M LiTFSI was obtained. This huge difference is mainly caused by the differences in viscosity as the values for the surface tension showed just little variations. However, it has to be mentioned that these values are just estimations of the influence of the electrolyte properties on the penetrability  $K$  obtained by applying Eq. 4. These values cannot be compared with measured

**Table 1** The influence of surface tension ( $\sigma$ ) and viscosity ( $\eta$ ) on the penetrability of PC–PYR<sub>14</sub>TFSI–0.3 M LiTFSI mixtures according to the Lucas–Washburn equation at 20 °C

PC content/ wt%	$\sqrt{\frac{\sigma}{2\eta}}/(\text{m s}^{-1})^{1/2}$
0	0.34
20	0.70
50	1.49
80	1.97
100	2.46

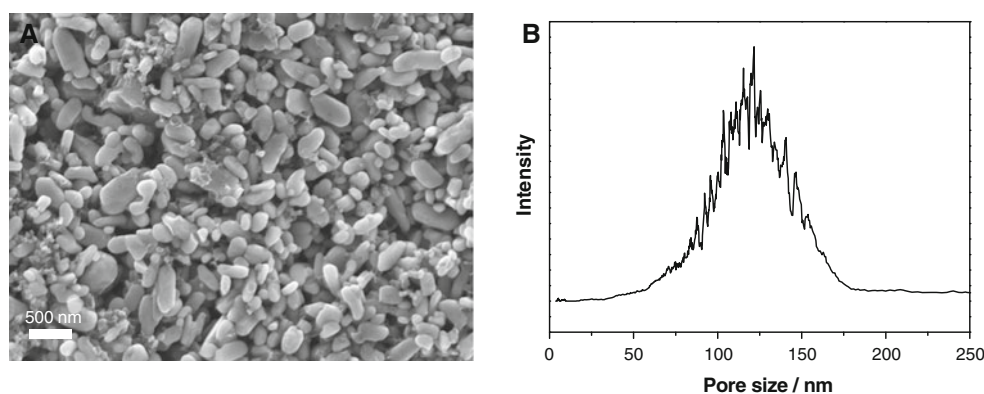
values of  $K$  because Eq. 4 does not include all the variables needed for the complete description of the penetrability according to the Lucas–Washburn equation (Eq. 1b).

To investigate the influence of the electrode properties on the wetting dynamics, the Lucas–Washburn equation (Eqs. 1a and 1b) was used. First, the LiFePO<sub>4</sub> composite electrodes were characterized in terms of morphology, porosity and pore size distribution in order to obtain an average value of the interparticle distances (pore size), which roughly corresponds to the capillary radius used in the Lucas–Washburn equation. In Fig. 2a, a typical SEM image of the electrodes is shown. The morphology of the electrodes is dominated by the oblong and rounded LiFePO<sub>4</sub> particles with a length of up to 600 nm. A SEM image with lower magnification (not shown) revealed good homogeneity of the electrodes, which is important for reproducibility of the wetting experiments. The pore size distribution of the electrodes, given in Fig. 2b, was rather narrow with a maximum at ca. 125 nm, corresponding to a “capillary radius” of 62.5 nm. This value corresponds quite well with the gaps between the LiFePO<sub>4</sub> particles visible in the SEM image. The porosity of the electrodes was measured to be 53.2 %.

Fries et al. showed that the Lucas–Washburn equation can be used for the description of capillary rise just up to 10 % of the maximum reachable height with a reasonable error. Above 10 %, the influence of gravity on the wetting kinetics, which is neglected in the Lucas–Washburn equation, becomes too dominant [23]. To confirm that the Lucas–Washburn equation can be applied for our experiments, the maximum expected height of capillary rise  $h_{\text{max}}$



**Fig. 2** **a** SEM image and **b** pore size distribution of LiFePO<sub>4</sub> composite electrodes. The composition of the electrodes was 88 wt% carbon-coated LiFePO<sub>4</sub>, 6 wt% carbon black and 6 wt% PVdF binder. The mass loading of the electrodes was ca. 10 mg cm<sup>-2</sup>



was calculated using Eq. 5, where  $g$  is the gravitational acceleration.

$$h_{\max} = \frac{2\sigma \cos \theta}{r\rho g} \quad (5)$$

The maximum imbibition height for the electrolyte with the solvent mixture of 50 wt% PC and 50 wt% IL was calculated to be 15.5 m using the capillary radius of 62.5 nm (from the pore size distribution) and a conservative estimate of the contact angle of 80° [the larger the contact angle, the smaller will be the maximum height (see Eq. 5)]. Hence, the investigated electrodes with a height of 1.8 cm come under the 10 % criteria of the applicability of the Lucas–Washburn equation [23], and therefore, this equation can be used for our experiments.

The mass increase  $\Delta m$  measured with the tensiometer was converted into a height increase using Eq. 2. The cross section  $A$  of the electrodes was 1.341 mm<sup>2</sup> and the porosity 53.2 %. The density of the electrolyte mixtures shown in Fig. 1b displayed a nearly linear dependence on the PC fraction of the investigated PC–PYR<sub>14</sub>TFSI–0.3 M LiTFSI mixtures. PYR<sub>14</sub>TFSI–0.3 M LiTFSI showed the highest density of 1.422 g cm<sup>-3</sup>, whereas PC–0.3 M LiTFSI displayed the lowest density of 1.240 g cm<sup>-3</sup>. The density of the mixtures deviated slightly from the arithmetic averages to lower values. With the calculated values for the height increase, the penetrability  $K$  was then obtained from a linear regression in an  $h$  versus  $t^{1/2}$  plot using Eq. 1a.

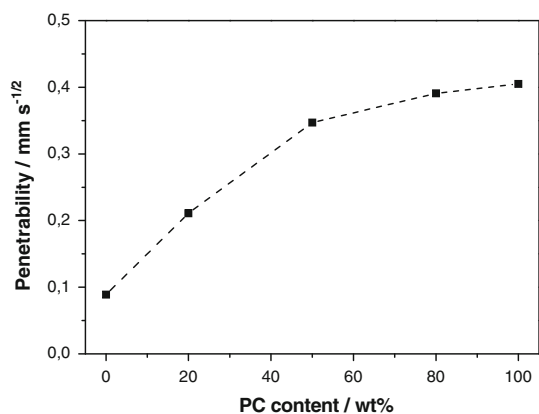
The results are shown in Fig. 3 and Table 2. It can be seen that the penetrability increased dramatically with increasing PC content from 0.089 mm s<sup>-1/2</sup> for PYR<sub>14</sub>TFSI–0.3 M LiTFSI to 0.405 mm s<sup>-1/2</sup> for PC–0.3 M LiTFSI. When 20 wt% IL in PYR<sub>14</sub>TFSI–0.3 M LiTFSI was substituted by PC, the penetrability was more than 2 times higher than that of the pure IL-based electrolyte. Substituting 50 wt% IL by PC led to an increase in penetrability by a factor of almost 4. However, upon further substitution of IL by PC, the penetrability increased only slightly from 0.347 to 0.405 mm s<sup>-1/2</sup>. The factor of 4.5 between the fastest wetting kinetics for PC–0.3 M LiTFSI and the slowest for PYR<sub>14</sub>TFSI–0.3 M LiTFSI

was in the same order of magnitude as expected from the obtained results based on the electrolyte properties only (see above). Nevertheless, the measured difference in penetrability was smaller than the estimated factor of 7. This difference can be explained by the interaction between the electrode and the electrolyte. The composite electrode can be expected to be rather hydrophobic as it contains carbon-coated LiFePO<sub>4</sub>, carbon black and PVdF as binder. PYR<sub>14</sub>TFSI also has a hydrophobic character, while propylene carbonate is rather hydrophilic. Therefore, a lower (average) contact angle between the surface of the pores of the electrode and the electrolytes with a high ionic liquid content compared to those with a high PC content is expected. According to Eq. 1b, a lower contact angle results in a higher penetrability and hence might explain the lower factor between the penetrability of PC–0.3 M LiTFSI and PYR<sub>14</sub>TFSI–0.3 M LiTFSI obtained by the experiment. The factor of 4.5 in penetrability difference translates to a difference in wetting time of ca. 20 times since the wetting time is proportional to the inverse square of the penetrability (Eq. 6).

$$t = \frac{h^2}{K^2} \quad (6)$$

This result shows that the composition of the electrolyte has a dramatic influence on the wetting kinetics of electrodes.

The tensiometer method can be considered as a standard method for the investigation of wetting dynamics. However, a huge excess of electrolyte is necessary for this measurement, which is not present in real systems. Therefore, a second method based on impedance spectroscopy measurements, which is closer to real systems, was explored. The impedance of Ni/LiFePO<sub>4</sub> (two-electrode) cells containing the different electrolyte mixtures was recorded over time without applying any current. In Fig 4a, the change in impedance over time for a cell containing the electrolyte with 50 wt% PC and 50 wt% PYR<sub>14</sub>TFSI is shown as an example. It can be seen that the impedance of this cell was stabilizing after 18 h. This time was interpreted as the time needed for the complete wetting



**Fig. 3** Penetrability of PC–PYR<sub>14</sub>TFSI–0.3 M LiTFSI mixtures into LiFePO<sub>4</sub> composite electrodes. The composition of the electrodes was 88 wt% carbon-coated LiFePO<sub>4</sub>, 6 wt% carbon black and 6 wt% PVdF binder. The mass loading of the electrodes was ca. 10 mg cm<sup>-2</sup>. The dashed lines are only guides to the eye

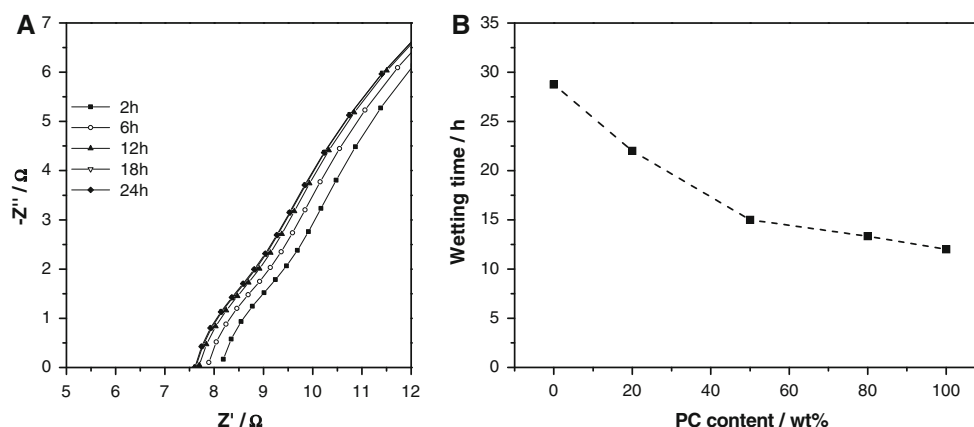
**Table 2** The penetrability  $K$  of PC–PYR<sub>14</sub>TFSI–0.3 M LiTFSI mixtures in LiFePO<sub>4</sub> composite electrodes obtained from sorption measurements using a tensiometer at 20 °C

PC content/wt%	$K/(\text{mm s}^{-1/2})$
0	0.089
20	0.211
50	0.347
80	0.394
100	0.405

of the LiFePO<sub>4</sub> composite electrode. The same measurement was also conducted for the other four electrolytes, and the average values of the wetting time are shown in Fig. 4b. It can be seen that the wetting time dropped significantly with increasing PC content. The wetting time obtained with the electrolyte based on pure IL was ca. 29 h and decreased upon substitution of 20 and 50 wt% IL by PC to 22 h and 15 h, respectively. However, a further increase in the PC content did not have a pronounced influence on the wetting time. The wetting times obtained with this method showed the same trend like the ones (calculated from the penetrability) obtained with the tensiometer. However, the factor between the longest wetting time for the electrolyte containing pure IL and the shortest for the one based on pure PC was smaller than expected from the tensiometer measurements. The existence of a difference in the factors in wetting time between the fastest and slowest wetting electrolyte is not surprising and can be explained by the different setup of the two methods. In the case of the tensiometer, no separator was acting as electrolyte reservoir leading to equal “availability” of the different electrolytes. For the impedance method, a separator soaked with electrolyte was used as reservoir. Therefore, the results of this experiment come from the

combined contribution of separator and electrode on the wetting process. The Whatman GF/D glass fiber separator used here should be rather hydrophilic and, therefore, releases electrolytes with a high content of hydrophobic PYR<sub>14</sub>TFSI easier than electrolytes with a high content of hydrophilic PC. This “separator effect” should lead to relatively shorter wetting times for the high IL-content electrolytes as compared to the results obtained with the tensiometer, which are reflecting only the influence of the electrode. Furthermore, the flow direction could play a role. It was parallel to the current collector in case of the tensiometer experiments, whereas it was perpendicular for the impedance experiments in the Swagelok cells leading to much shorter capillaries limited by the thickness of the electrodes. Shorter capillaries could mean that inertia effects played a bigger role here, which are neglected by the Lucas–Washburn equation.

The results reported above give also interesting information about the methods suitable to investigate the wetting time of porous electrodes. As shown, the use of both methods led to the same trend, indicating that they can both be used to study wetting dynamics in porous electrodes. Nevertheless, there are some general differences between the two methods. First of all, the timescale of the two experiments is very different. The observation time for the experiments using the tensiometer is much shorter than that of the impedance spectroscopy measurements. This is due to the fact that in the tensiometer experiments the electrolyte front almost reached the top of the 1.8-cm high electrode within 20 min with PC–0.3 M LiTFSI while it took more than 10 h till the impedance of the 74.5-μm-thick electrode stabilized. This time difference cannot be explained solely with the better availability of electrolyte due to its large excess and the absence of a separator for the tensiometer measurements. Therefore, it is reasonable to assume that the huge difference in absolute wetting time comes from a different degree of wetting. Wetting of bigger pores is generally faster (see Eq. 1b) than the wetting of smaller pores. Hence, with the tensiometer only the (complete) wetting of the bigger pores is observed. In the case of the investigated LiFePO<sub>4</sub> electrodes, the bigger pores (e.g., >75 nm) contributed the most (>95 %) to the free volume of the electrode (see Fig. 2b). Thus, also the filling of the bigger pores contributed the most to the measured weight increase. On the other hand, small pores should have a noticeable influence on the impedance (see Eq. 3) of the electrode because of their relatively higher contribution to the total surface area compared to their contribution to the total volume. Furthermore, a “complete” wetting of the electrode is necessary for the impedance to stabilize because it is a rather sensitive technique. Therefore, the results obtained with the impedance method reflect better the complete wetting of the



**Fig. 4** **a** Example for the evolution of the complex impedance of a Ni/LiFePO<sub>4</sub> composite electrode (two-electrode) cell with time. PC–PYR<sub>14</sub>TFSI–0.3M LiTFSI (50 wt% PC and 50 wt% PYR<sub>14</sub>TFSI) was used as electrolyte. **b** Wetting time of LiFePO<sub>4</sub> composite electrodes by PC–PYR<sub>14</sub>TFSI–0.3M LiTFSI mixtures with different PC content

electrode and should thus have the bigger practical relevance.

Even though the tensiometer has the advantages that the obtained results can be more easily compared with results reported in the literature and that the wetting of single-battery components, such as electrodes or separator, can be studied separately, impedance spectroscopy measurements might be preferred because they are much closer to real systems as also the wetting of the smaller pores is influencing the results. Additionally, these measurements are easy to conduct and require only standard electrochemical equipment. However, it is important to carry out impedance spectroscopy measurements on the one hand under temperature control, since the impedance is quite sensitive to temperature, and on the other hand using very homogeneous electrodes to obtain reproducible results. Finally, we have to point out that the results obtained with both methods are difficult to compare with results obtained for other electrode–electrolyte combinations due to the many factors influencing the wetting behavior of an electrode, especially if the results were obtained via an impedance method where additional factors such as the separator come into play. Therefore, the values of penetrability and wetting time presented in this work should rather be taken as a guideline than being interpreted quantitatively.

#### 4 Conclusions

In this manuscript, we compared two different techniques, employing a tensiometer or impedance spectroscopy, to investigate the wetting dynamics of LiFePO<sub>4</sub> composite electrodes. The trend obtained for both methods was the same. Substitution of 20 or 50 wt% of IL by PC in

derived from impedance experiments (see A). The time needed for the impedance to stabilize was interpreted as the time needed to wet the LiFePO<sub>4</sub> composite electrodes. The experiments were carried out at 20 °C. The *dashed line* is only a guide to the eye

PYR<sub>14</sub>TFSI–0.3 M LiTFSI strongly increased the speed of wetting. Further substitution only slightly decreased the wetting time. Therefore, both methods can be used as a tool to find an optimal electrolyte composition regarding wetting time, which is a cost factor in the manufacturing of electrochemical energy storage devices. This is of special interest when the use of ionic liquids as electrolyte component is considered in order to increase the intrinsic safety of the electrolyte as ILs display considerably higher viscosities than standard electrolyte solvents.

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